Vanadium complexes containing amido functionalized cyclopentadienyl ligands

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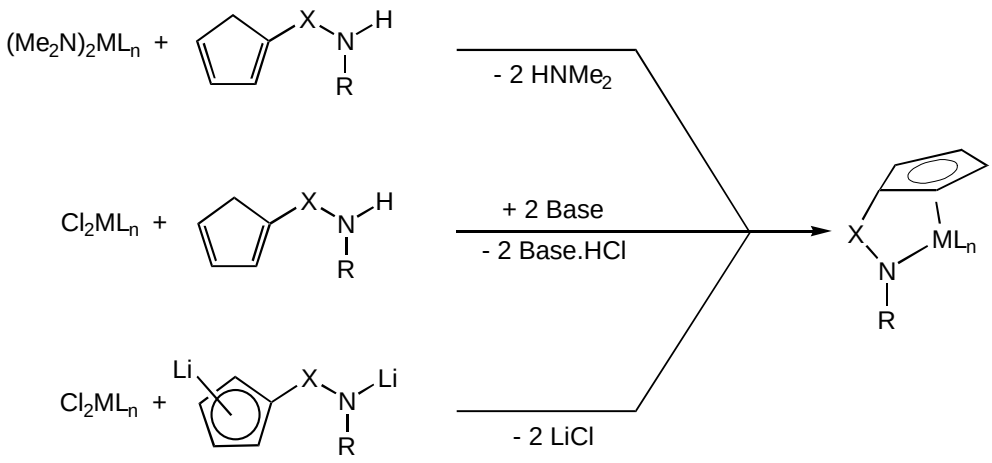
Chapter 2

Synthesis of vanadium(V) complexes containing amido functionalized cyclopentadienyl ligands

2.1 Introduction

Several methods have been reported to introduce amido functionalized cyclopentadienyl (Cp-amido) ligands on a metal center. Ligand introduction by amine elimination (starting from a metal-amido complex)[1] or HCl elimination (starting from a metal-chloro complex)[2] uses a neutral ligand precursor which is deprotonated by the metal-amido or metal-chloride group (Scheme 1). Lithiation of the neutral ligand precursor and subsequent reaction of the resulting di-anion with a metal chloride is probably one of the most frequently used methods (Scheme 1).[3]

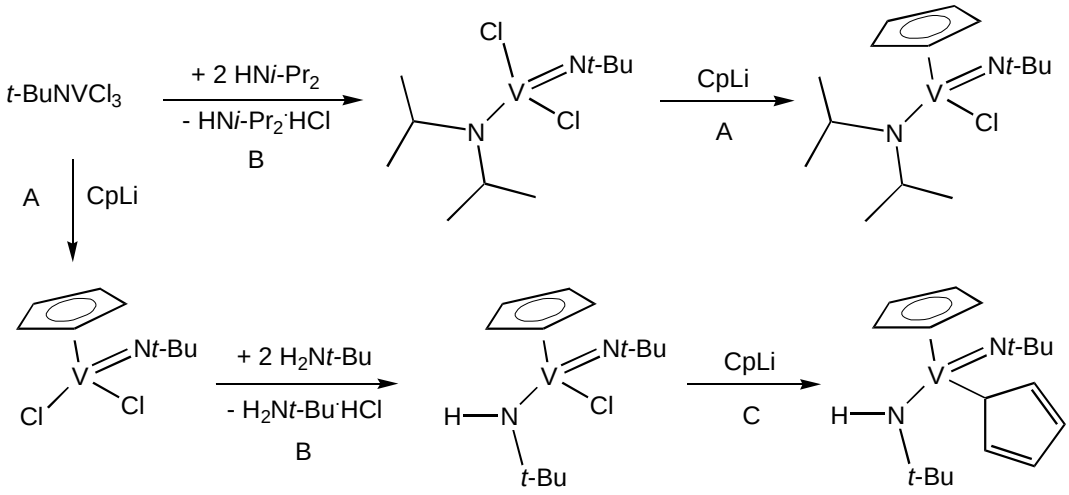


Scheme 1

So far, research on complexes with Cp-amido ligands has mainly been focussed on the group 4 metals.[4] Research on Cp-amido complexes of group 5

metals is limited to the synthesis of (η^5,η^1-$C_5H_4SiMe_2NPh$)$M(NMe_2)_3$ (M = Nb, Ta), and (η^5-$C_5Me_4CH_2N$*t*-Bu)TaCp* (Cp* = η^5-C_5Me_5).[5] The NMe_2 complexes are synthesized by amine elimination from $M(NMe_2)_5$; the Cp* complex is formed by intramolecular coupling of one of the Cp* ligands of [Cp^*_2Ta(N*t*-Bu)][$B(C_6F_5)_4$] with the imido ligand. Related vanadium chemistry has not been reported.

Although no Cp-amido vanadium complexes are known, vanadium(V) complexes with both a cyclopentadienyl and an amido ligand, but without a link between them, have been reported (Scheme 2).[6] The Cp ligand was introduced on vanadium(V) using CpLi (reactions A), the amido ligands by HCl elimination (reactions B). Since the Cp vanadium amido chloro complexes react with CpLi (reaction C), it is preferred to introduce the Cp ligand prior to the amido ligand.



Scheme 2

This chapter describes the synthesis and characterization of Cp-amido vanadium(V) complexes with an additional imido ligand. Imido ligands are often used in vanadium(V) chemistry, since the good π-donating capabilities of these ligands stabilize the high oxidation state of the metal center. Introduction of the Cp-amido ligand by amine elimination was investigated using the series of complexes *t*-$BuNV(NMe_2)_nCl_{3-n}$ (n = 1, 2, 3) as starting materials. This yielded the complexes (Cp-amido)VCl(N*t*-Bu), from which a series of alkyl complexes

was synthesized. Cp-amido vanadium(V) imido complexes with an aromatic substituent on the imido ligand were obtained by exchange of the imido ligand after introduction of the Cp-amido ligand. In addition, several Cp vanadium(V) amido complexes, without a link between the Cp and amido functionality, were synthesized, which can serve as comparison.

2.2 Results and discussion

2.2.1 Synthesis of imido vanadium(V) amido complexes

The imido tris-amido vanadium complex (*t*-BuN)V(NMe_2)$_3$ (**1**) is obtained by reacting (*t*-BuN)VCl_3 (**4**) with three equivalents of $LiNMe_2$. Complex **1** is an oil and can be purified by vacuum transfer. The di-amido and mono-amido complexes (*t*-BuN)VCl(NMe_2)$_2$ (**2**) and (*t*-BuN)VCl_2(NMe_2) (**3**) can also be synthesized by reaction of **4** with $LiNMe_2$ (using two and one equivalents of $LiNMe_2$ respectively) but in a low isolated yield (<50%). A more convenient route for their synthesis is by the comproportionation of **1** and **4** (Equations 1a, b). These ligand redistributions are fast: reactions in C_6D_6 on NMR tube scale show that full conversion is reached within five minutes at room temperature. For comparison, the comproportionation of the vanadium(IV) complexes VCl_4 and V(NEt_2)$_4$ takes five hours at 100^{o}C to go to completion.[7] A comproportionation reaction on preparative scale was performed for **2** and resulted in an 81% isolated yield.

2 (*t*-BuN)V(NMe_2)$_3$ (**1**) + (*t*-BuN)VCl_3 (**4**) ⟶ 3 (*t*-BuN)VCl(NMe_2)$_2$ (**2**) (1a)

(*t*-BuN)V(NMe_2)$_3$ (**1**) + 2 (*t*-BuN)VCl_3 (**4**) ⟶ 3 (*t*-BuN)VCl_2(NMe_2) (**3**) (1b)

The ^{1}H NMR spectra of **1** and **2** show only one singlet for the NMe_2 groups over the temperature range of -70 to +30^{o}C, indicating rapid rotation of the NMe_2 fragment around the V-N(amido) bond. For **3** the NMe_2 resonance appears as two singlets at -70^{o}C (both with the intensity of one Me-group), which coalesce at 80^{o}C into one broadened resonance. Since no steric effects

influence the rotation around the V-N(amido) bond, the higher rotational barrier of **3** (compared to **1** and **2**) is probably caused by a stronger N(amido) to V π-donation due to the greater electron deficiency of the vanadium center in **3**.

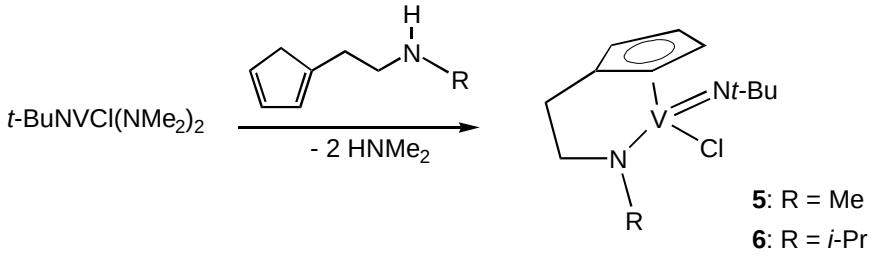
The ^{51}V NMR spectra of **1** - **4** show that substitution of a chloride by an amido ligand results in an upfield shift of the vanadium resonance. Starting from the imido vanadium tri-chloride **4** (^{51}V NMR: δ 3 ppm) substitution of one chloride for a NMe_2 group results in an upfield shift in the ^{51}V NMR of about 160 ppm (**3**: δ -153 ppm): substitution of a second chloride results in a further upfield shift of 130 ppm (**2**: δ -281 ppm). Comparable upfield shifts for the substitution of a chloride ligand for an amido ligand have been found in the series of vanadium(V) oxo complexes $OV(NMe_2)_nCl_{3-n}$ (n = 1, 2, 3),[8] and shows that the stronger π-donation of the amido group compared to the chloride increases the electron density on the metal.

2.2.2 Ligand introduction by amine elimination

We have introduced the Cp-amido ligand on vanadium(V) by amine elimination, using the vanadium(V) amido complexes **1** and **2** as starting materials. The reaction of **2** with $C_5H_5CH_2CH_2N(H)R$ (R = Me, *i*-Pr) in refluxing pentane resulted in the formation of (η^5,η^1-$C_5H_4CH_2CH_2NR$)VCl(N*t*-Bu) (**5**: R = Me; **6**: R = *i*-Pr, Scheme 3). The Cp-amido vanadium(V) complexes **5** and **6** crystallized readily from pentane solutions and were isolated in yields of 74 and 83% respectively.

The vanadium center in the complexes **5** and **6** is asymmetric and the four Cp protons and the four protons of the ethylene bridge all appear in the ^{1}H NMR as separate multiplets. The NMe resonance in **5** (4.0 ppm) appears downfield from the corresponding resonance in the ligand precursor $C_5H_5CH_2CH_2N(H)Me$ (2.3 ppm). In **6** the two methyls of the N*i*-Pr group are inequivalent (1.01 and 0.98 ppm), with a chemical shift comparable to the corresponding resonance in the ligand precursor $C_5H_5CH_2CH_2N(H)$*i*-Pr (0.95 ppm). The methine proton of the *i*-Pr group appears much more downfield in **6** than in the ligand precursor (6.0 ppm in **6**, 2.6 ppm in ligand precursor). Similar

downfield shifts are observed in the Cp-amido titanium(IV) complexes $[C_5H_4(CH_2)_nN\textit{i}\text{-Pr}]TiCl_2$ (n = 2, 3).[2]



Scheme 3

Reaction of the imido vanadium tris-amido complex **1** with the ligand precursor $C_5H_5CH_2CH_2N(H)\textit{i}\text{-Pr}$ in C_6D_6 at 75°C showed rapid formation of $HNMe_2$. After 3 hours, resonances of **1** and the ligand precursor were no longer observed in the ^{1}H NMR spectrum. Instead, the product (η^5,η^1-$C_5H_4CH_2CH_2N\textit{i}\text{-Pr}$)V($NMe_2$)(N*t*-Bu) was observed, together with unknown impurities. Further heating at 75°C caused the product to decompose.

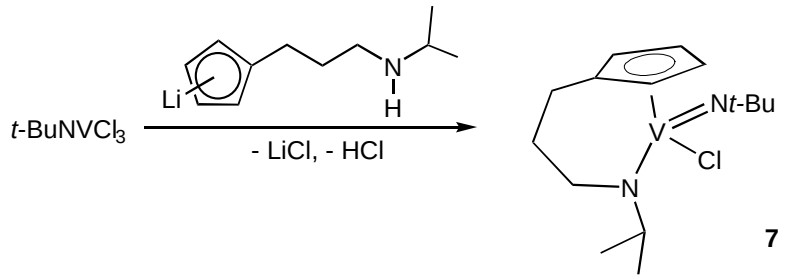
Ligand introduction can also be achieved by a combination of amine and HCl elimination, using the mono-amido complex **3** as a starting material. When the reaction of **3** with the ligand precursor $C_5H_5(CH_2)_2N(H)\textit{i}\text{-Pr}$ was performed in the presence of an extra added base (Et_3N, in C_6D_6), ^{1}H NMR showed the formation of the Cp-amido complex **6**. However, when we attempted this reaction on a preparative scale, **6** was obtained as an impure sticky solid, which could not be purified by crystallization.

2.2.3 Ligand introduction by salt metathesis

The Cp-amido ligand with an ethylene bridge between the Cp and amido functionality can easily be introduced on vanadium(V) by amine elimination from the bis-amido complex **2**. However, introduction of a Cp-amido ligand with a propylene bridge proved much more difficult. The reaction of **2** with $C_5H_5(CH_2)_3N(H)\textit{i}\text{-Pr}$ on NMR scale (C_6D_6) showed no conversion, even after prolonged heating at 75°C. Higher temperatures resulted in decomposition of

the ligand and **2**, therefore another method was used for the synthesis of Cp-amido vanadium(V) complexes with a propylene bridge.

When a THF-d_8 solution of the ligand precursor $C_5H_5(CH_2)_3N(H)i$-Pr was treated with one equivalent of Me_3SiCH_2Li, ^{1}H NMR showed the deprotonation of the Cp moiety (two triplets are observed for the four Cp protons) and Me_4Si was generated. Addition of an extra equivalent of Me_3SiCH_2Li generated more Me_4Si, but no resonances for the Cp-amido ligand were observed, instead, the solution became turbid. Although the deprotonation of the Cp moiety is fast (complete in less than five minutes), deprotonation of the amido functionality takes more than half an hour. Similar observations were made when the ethylene bridged ligand precursor $C_5H_5(CH_2)_2N(H)i$-Pr was deprotonated by Me_3SiCH_2Li.



7

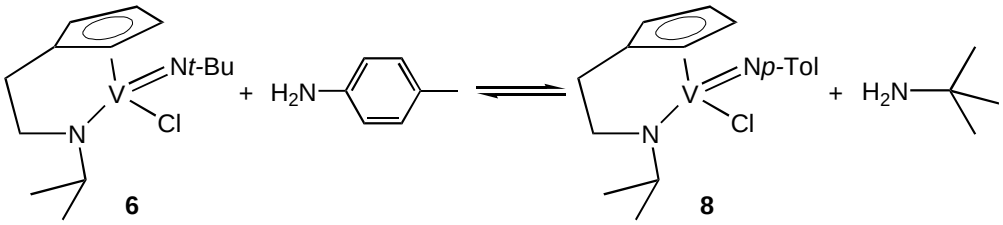
Scheme 4

For ligand introduction by salt metathesis the imido vanadium tri-chloride **4** was used as a starting material. Reaction of the mono-lithium salt $[C_5H_4(CH_2)_3N(H)i$-Pr]Li with **4** resulted in the formation of (η^5,η^1-$C_5H_4CH_2CH_2CH_2Ni$-Pr)VCl(N*t*-Bu) (**7**), indicating the additional elimination of HCl (Scheme 4). The Cp-amido complex **7** was isolated as a red oil in a low yield (37%) after extraction with pentane. Large amounts of pentane-insoluble paramagnetic (by ^{1}H NMR) compounds were formed as well. The yield of **7** did not improve when its synthesis was carried out in the presence of the base Et_3N.

2.2.4 Variation of the imido substituent

Introduction of the Cp-amido ligand on vanadium(V) bearing an imido ligand with an aromatic substituent could not be performed using the amine elimination route described above, since the synthesis of imido vanadium(V) amido starting complexes from (*p*-TolN)VCl_3 was unsuccessful. An alternative synthetic procedure is the exchange of the *t*-Bu imido ligand after introduction of the Cp-amido ligand.

It was reported that the reaction of (*t*-BuN)$VCpCl_2$ with one equivalent of the aniline $ArNH_2$ (Ar = 2,6-(*i*-Pr)$_2$-C_6H_3) yields (ArN)$VCpCl_2$ and *t*-$BuNH_2$, after heating at 75^{o}C for 10 days ($C_2H_4Cl_2$).[9] When the *t*-Bu imido vanadium complex **6** was reacted with *p*-TolNH_2 in a sealed NMR tube (C_6D_6), resonances for a new complex and *t*-$BuNH_2$ appeared after the mixture was heated to 75^{o}C. However, even after prolonged heating full conversion was not observed. Apparently the reaction reaches an equilibrium where about 50% of **6** is converted.



6 **8**

Scheme 5

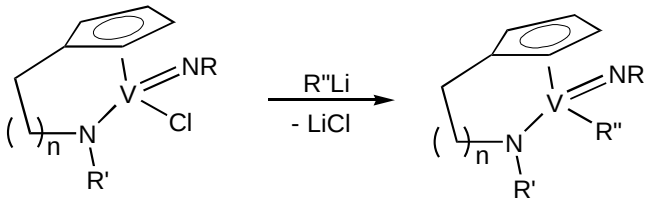
The complex (η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)VCl(N*p*-Tol) (**8**, Scheme 5) was obtained on preparative scale from **6** and *p*-TolNH_2 in refluxing toluene in a 78% isolated yield. In this case the equilibrium shown in Scheme 5 could be driven to the right by using a small excess of *p*-TolNH_2 and by degassing the reaction mixture periodically to remove the volatile *t*-$BuNH_2$.

The imido exchange has little effect on the ^{1}H and ^{13}C NMR resonances of the Cp-amido ligand. In the ^{51}V NMR spectrum the *p*-Tol imido complex **8**

appears 95 ppm downfield from the *t*-Bu imido complex **6**, probably because of the better electron donating properties of the *t*-Bu substituent. The difference is much smaller than for the corresponding imido vanadium(V) tri-chlorides, where (*p*-TolN)VCl_3[10] appears 300 ppm downfield from (*t*-BuN)VCl_3.[11]

2.2.5 Synthesis of Cp-amido vanadium(V) alkyl complexes

Reaction of the Cp-amido vanadium(V) chloro complexes **5** - **8** with lithium alkyls that do not contain β-H atoms yielded the vanadium(V) alkyls (Cp-amido)VR'(NR) (Scheme 6). Only the *t*-Bu imido vanadium methyl complex **10** was obtained as a crystalline solid, all other complexes were isolated as highly soluble dark red or brown oils. The *p*-Tol imido vanadium methyl complex **13** crystallized when it was refrigerated at -30°C, however, the crystals melted upon warming.



n	R	R'	R"	compound
1	*t*-Bu	Me	Me	**9**
		i-Pr	Me	**10**
			CH_2CMe_3	**11**
			CH_2CMe_2Ph	**12**
1	*p*-Tol	*i*-Pr	Me	**13**
2	*t*-Bu	*i*-Pr	Me	**14**

Scheme 6

The ^1H and ^{13}C NMR spectra of the alkyl complexes show that the resonances for the imido and Cp-amido ligands do not change significantly upon alkylation. The resonances for the alkyl groups show a characteristic broadening caused by the quadrupolar vanadium nucleus (see Chapter 1, section 1.5). In the ^1H NMR spectra the V-CH_3 resonance appears as a broadened singlet around 0.8 ppm with a line width at half height ($\Delta\nu_{1/2}$) of 7 Hz,

the V-CH_2 group appears more downfield (multiplet, 1.6 ppm). In the ^{13}C NMR spectra the V-C resonances are only observed at low temperatures, the V-CH_2 resonance also appears more downfield than the V-CH_3 resonance.

The alkyl complexes **10** - **12** were stable in C_6D_6 solution for several months at room temperature. However, heating the solutions led to slow decomposition as was seen by a color change of the solution from brown to purple (see below). The same product was formed for all three decompositions, however, the decompositions were not clean.

Attempts to synthesize a vanadium(V) alkyl complex by reaction of **6** with EtMgCl at low temperatures, led to the formation of a purple solution. After extraction of the reaction mixture with pentane, dark crystals were obtained which display the same ^1H NMR spectra as the thermolysis product described above.The product could not be purified by crystallization.

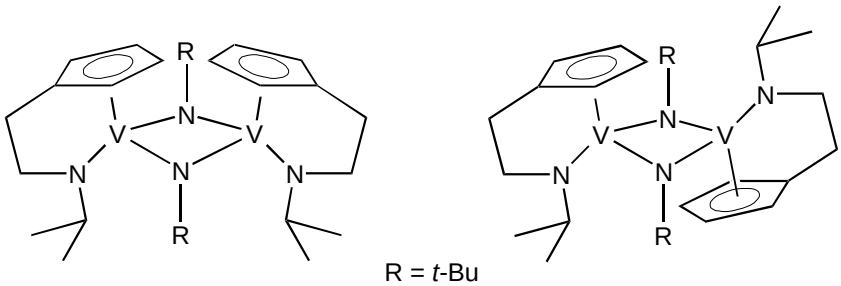


Figure 2: Two possible isomers of **15**.

In contrast to complexes **5** - **14** the thermolysis product has a plane of symmetry, as is seen from the ^1H and ^{13}C NMR spectra. We propose that this product is the vanadium(IV) dimer [(η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)V(μ-N*t*-Bu)]$_2$ (**15**). Similar vanadium(IV) dimers have been reported for the attempted alkylation of the vanadium(V) complexes (*t*-BuN)VCp(O*t*-Bu)Cl and (*p*-TolN)VCpCl_2.[10] These products, [Cp(*t*-BuO)V(μ-N*t*-Bu)]$_2$ and [CpClV(μ-N*p*-Tol)]$_2$, show a downfield shift in the ^{51}V NMR of 500 ppm compared to the starting complexes. The Cp-amido vanadium(IV) dimer **15** appears at +137 ppm, a downfield shift of 800 ppm compared to the Cp-amido vanadium(V) chloride **6**.

There are two possible isomers for **15**, as shown in Figure 2. From the work of Vroegop *et al*. on imido bridged titanium dimers it is known that isomer A is preferred when the bridging imido ligand has a *t*-Bu substituent,[13] and following this example we propose this structure for **15**.

2.2.6 Structure determination of **10**

The methyl complex **10** was recrystallized from pentane to yield dark red crystals suitable for X-ray structure determination. The structure (Figure 3) shows the η^5,η^1-bonding of the Cp-amido ligand. The V-Cg bond length (1.9835(15) Å; Cg = center of gravity of the Cp moiety) and V-N(amido) bond length (1.854(2) Å) are normal for vanadium(V).[6a,14] The planar geometry of the N(amido) and the linear geometry of the N(imido) reflects the π-donation of the nitrogen atom lone pairs. The V-N(imido) unit is more linear than that of other V(V)-(N*t*-Bu) complexes (V-N-C = 175.61(18)^o for **10**, reported V-N-C = 161 - 172^o),[6a,15] what could indicate a stronger π-donation than in reported complexes. However, the V-N(imido) bond length is slightly longer than in other complexes (V-N = 1.656(2) Å for **10**, reported V-N = 1.59 - 1.64 Å).[6a,14] The V-Me distance (2.103(3) Å) is somewhat longer than that of Li[(*t*-$Bu_3SiN)_2VMe_2$] (2.04 - 2.06 Å),[16] the only other V(V)-methyl complex that is structurally characterized. Proton H8 of the *i*-Pr group is pointing towards the metal center (V1···H8 = 2.84 Å), which is probably the reason for the observed downfield shift of this proton in the ^{1}H NMR spectrum.

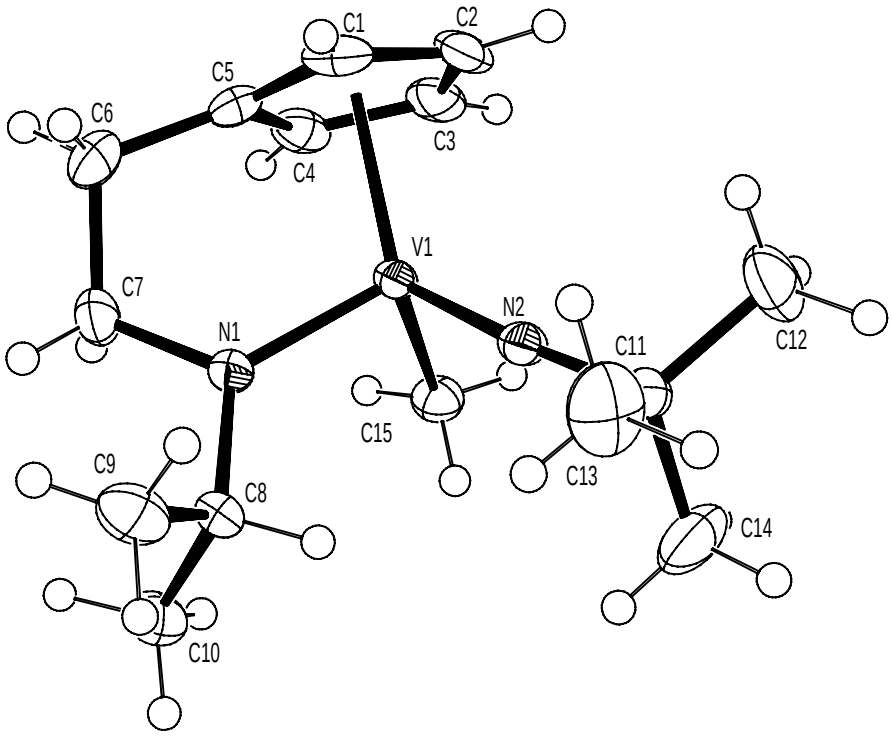


Figure 3: Crystal structure of **10**.

Table 1: Selected bond distances and angles in **10**.

V-N(1)	1.854(2)	Cg-V-N(1)	110.12(7)
V-N(2)	1.656(2)	Cg-V-N(2)	130.45(7)
V-C(15)	2.103(3)	Cg-V-C(15)	111.72(9)
V-Cg	1.9835(15)	N(1)-V-N(2)	105.78(10)
		C(15)-V-N(1)	96.10(11)
		C(15)-V-N(2)	96.87(12)
		V-N(2)-C(11)	175.61(18)

2.2.7 Complexes without a bridge between the Cp and amido functionality

In order to investigate the influence of the bridge between the Cp and amido functionality on the reactivity of the Cp-amido complexes (as will be described in Chapter 4), vanadium(V) complexes with a Cp and amido ligand without a link between them were synthesized for comparison. Preuss *et al.* synthesized the imido vanadium(V) complexes (*t*-BuN)V(η^5-C_5H_5)(NRR')Cl (R = *t*-Bu, R' = H; R = R' = *i*-Pr; Scheme 2).[6] We extended this chemistry by

introducing an aromatic substituent on the imido functionality, so that a comparison with the (Cp-amido)VX(N*p*-Tol) complexes is possible.

The two routes reported by Preuss *et al.* are shown in Scheme 2.[6] The best method is to introduce the amido ligand on (*t*-BuN)$VCpCl_2$, as this is the most selective. However, we observed that this route is not available for complexes with an aromatic substituent on the imido ligand, since (*p*-TolN)$VCpCl_2$ does not react with HN*i*-Pr_2. Therefore we used the second route described by Preuss *et al*, where the Cp ligand is introduced after introduction of the amido ligand.

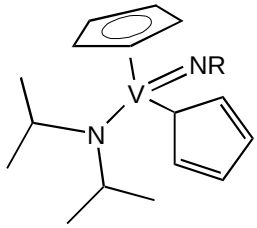
Reaction of (RN)VCl_3 (**4**: R = *t*-Bu; **16**: R = *p*-Tol) with two equivalents of HN*i*-Pr_2 yielded (RN)V(N*i*-Pr_2)Cl_2 (**17**: R = *t*-Bu; **18**: R = *p*-Tol) by HCl elimination. In a subsequent reaction with CpNa, the complexes (RN)VCp(N*i*-Pr_2)Cl (**19**: R = *t*-Bu; **20**: R = *p*-Tol) were formed. The ^{1}H and ^{13}C NMR resonances of the Cp and amido ligands in the *p*-Tol imido vanadium(V) complexes **18** and **20** are very similar to those of the reported *t*-Bu imido complexes **17** and **19**.[6] Table 2 shows the ^{51}V NMR characteristics of the complexes **4**, **16** - **20**. From it we can conclude that the electron density on the vanadium center increases when a Cp or an amido ligand is introduced. Furthermore, the electron donating capacity of the *t*-Bu substituent on the imido ligand is better than that of the *p*-Tol substituent, although this effect becomes less pronounced when the overall electron density on the metal center increases.

Table 2: ^{51}V NMR data of Cp vanadium(V) amido complexes.

Complex	chemical shift (ppm)	reference
(*t*-BuN)VCl_3 (**4**)	3	11
(*t*-BuN)V(N*i*-Pr_2)Cl_2 (**17**)	-173	6a
(*t*-BuN)VCp(N*i*-Pr_2)Cl (**19**)	-665	6a
(*p*-TolN)VCl_3 (**16**)	305	10
(*p*-TolN)V(N*i*-Pr_2)Cl_2 (**18**)	-67	this work
(*p*-TolN)VCp(N*i*-Pr_2)Cl (**20**)	-591	this work

The Cp vanadium(V) chloro complexes **19** and **20** react with CpNa, and when their synthesis was attempted with an excess of CpNa the bis-Cp

complexes (RN)VCp_2(N*i*-Pr_2) (**21**: R = *t*-Bu; **22**: R = *p*-Tol) were isolated. Preuss *et al.* synthesized the bis-Cp complexes (*t*-BuN)VCp_2X (X = NH*t*-Bu, O*t*-Bu),[6b,17] and showed that these complexes contain one η^1-bonded Cp ligand and one that is η^5-bonded (determined by ^{1}H NMR spectroscopy at -140^{o}C). Low temperature ^{1}H NMR measurements on **21** and **22** were limited by the minimum temperature of the used NMR probe (-100^{o}C). Nevertheless, since these NMR spectra resemble the -100^{o}C ^{1}H NMR spectrum of (*t*-BuN)VCp_2(O*t*-Bu), we assume a similar bonding type of the Cp ligands in **21** and **22** (Figure 4).



21: R = *t*-Bu
22: R = *p*-Tol

Figure 4: Proposed structure of **21** and **22**.

Reaction of the Cp vanadium(V) chloro complexes **19** or **20** with MeLi yielded the corresponding methyl complexes, (RN)VCp(N*i*-Pr_2)Me (**23**: R = *t*-Bu; **24**: R = *p*-Tol). In both methyl complexes the resonances for the imido, amido and Cp ligand in ^{1}H and ^{13}C NMR do not shift significantly compared to the corresponding chlorides. The ^{1}H NMR resonance for the V-CH_3 (δ 0.8 ppm, $\Delta\nu_{½}$ 15Hz) has the same chemical shift as the (Cp-amido)VCH_3(NR) complexes **9**, **10**, **13** and **14**, but is more broadened. The ^{51}V NMR resonances (δ -600 ppm, $\Delta\nu_{½}$ 350Hz) are comparable to the other methyl complexes.

2.3 Conclusions

Vanadium(V) imido complexes with Cp-amido ligands are best synthesized by amine elimination from (*t*-BuN)$V(NMe_2)_2Cl$. From this reaction (Cp-amido)VCl(N*t*-Bu) complexes were isolated in good yields when a ligand is used with an ethylene bridge between the Cp and amido functionality. However,

the route is not versatile and Cp-amido vanadium(V) complexes with a propylene bridge between the Cp and amido functionality could only be obtained by salt metathesis. Reaction of (Cp-amido)VCl(N*t*-Bu) complexes with aniline yielded Cp-amido vanadium(V) imido complexes with an aromatic substituent on the imido functionality. These complexes are not available using the amine elimination route, since the starting complex (*p*-TolN)V(NMe_2)$_2$Cl could not be obtained.

Stable Cp-amido vanadium(V) alkyl complexes were only obtained for alkyl ligands that do not contain a β-H atom. The crystal structure of ($C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*t*-Bu) shows that the Cp-amido ligand binds to the vanadium center in a η^5,η^1-fashion, with strong π-donation from the nitrogen atom, making the ligand an 8-electron donor.

For the synthesis of Cp vanadium(V) amido complexes in which there is no link between the Cp and amido ligand, two routes have been described in literature. Introduction of the Cp ligand by salt metathesis and subsequent introduction of the amido ligand by HCl elimination is prefered, since it is selective in forming (*t*-BuN)VCp(N*i*-Pr_2)Cl. Introduction of the Cp- ligand after the amido ligand is introduced is less selective, and formation of bis-Cp complexes has been observed. Unfortunately, only this last route yields Cp vanadium(V) amido complexes with a *p*-Tol imido substituent.

2.4 Experimental

General considerations

All experiments were performed under nitrogen atmosphere using standard glove-box and Schlenk line techniques. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use (C_6D_6, C_7D_8, THF-d_8). Pentane, hexane, ether, THF and toluene were distilled from Na or Na/K alloy before use. The following compounds were prepared according to literature procedures: $C_5H_5(CH_2)_nNHR$ (n = 2, R = Me, *i*-Pr; n = 3, R = *i*-Pr),[18] (*t*-BuN)VCl_3 (**4**),[11] (*p*-TolN)VCl_3 (**16**),[10] (*t*-BuN)V(N*i*-Pr_2)Cl_2 (**17**)[6a] and (*t*-BuN)VCp(N*i*-Pr_2)Cl (**19**).[6a] Me_3CCH_2Li, Me_3SiCH_2Li and $PhMe_2CCH_2Li$ were prepared by refluxing the corresponding chlorides with 3 equivalents of lithium metal overnight, followed by recrystallization from hexane. $HNMe_2$, 40% in H_2O (Merck), BuLi, 2.5 M in hexane (Acros), MeLi (Aldrich), *p*-$TolNH_2$ (Aldrich), and HN*i*-Pr_2 (Acros) were used as received. NMR spectra were run on Varian Gemini 200, VXR-300 and VXR-

500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to TMS, using residual solvent resonances as internal reference. ^{51}V NMR chemical shifts are reported in ppm relative to $VOCl_3$, which is used as an external reference. Coupling constants (J) and line widths at half height ($\Delta\nu_{½}$) are reported in Hz. IR spectra were recorded on a Mattson Galaxy 4020FT-IR spectrophotometer. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of (*t*-BuN)V(NMe_2)$_3$ (**1**)

Two 1L three neck flasks were connected with a rubber tube. One flask was charged with 150 g of NaOH pellets, and equipped with a dropping funnel (without a pressure equilizer) containing 20 mL of a 40% solution of $HNMe_2$ in H_2O (0.16 mol); the other flask was charged with 400 mL of toluene which was cooled to -30^{o}C. The system was put under a reduced pressure (~0.1 bar) and the amine solution was added to the NaOH pellets at such a rate that the pressure did not exceed 0.8 bar. When all amine solution was added and the pressure had dropped back to ~0.1 bar, the two flasks were filled with N_2 gas and disconnected. Slowly 50 mL 2.5 mL BuLi in hexane (0.13 mol) was added to the cooled toluene solution, which was stirred for half an hour at -30^{o}C. An orange solution of 9.9 g of **4** (43 mmol) in 80 mL of toluene was added in five minutes at -30^{o}C. The solution turned brown upon addition and was stirred overnight at room temperature, after which all volatiles were removed *in vacuo*. The resulting red oil was stripped from residual toluene by addition of 2 x 50 mL of hexane and 2 x 50 mL of pentane and subsequent removal *in vacuo*. Extraction of the red oil with 2 x 100 mL of pentane, followed by removal of the solvent *in vacuo* yielded 9.18 g of a red oil. Crude yield: 36 mmol (83%). ^{1}H NMR showed small amounts of impurities in the region of 0 - 4 ppm. This material is of sufficient purity to use in the subsequent synthesis of **2**, but can be further purified by vacuum transfer if desired.

^{1}H NMR (200 MHz, C_6D_6, 25^{o}C): δ 3.43 (s, 18H, NCH_3), 1.38 (s, 9H, *t*-Bu). *$^{13}C\{^{1}H\}$ NMR* (50.3 MHz, C_6D_6, 25^{o}C): δ 50.0 (br, NCH_3), 31.8 (CH_3 of *t*-Bu), C_q of *t*-Bu not observed. *^{51}V NMR* (78.9 MHz, C_6D_6, 25^{o}C): δ -267 (t, $J_{V\text{-}N}$ = 84). *IR (neat)*: 594 (w), 621 (w), 665 (w), 687 (w), 806 (w), 955 (s), 1047 (s), 1119 (s), 1159 (s), 1211 (s), 1236 (s), 1354 (s), 1412 (s), 1445 (s), 2764 (s), 2807 (s), 2845 (s), 2890 (s), 2918 (s), 2967 (s) cm^{-1}.

Synthesis of (*t*-BuN)VCl(NMe_2)$_2$ (**2**)

In 40 mL of pentane 1.56 g (6.1 mmol) of **1** and 0.70 g (3.1 mmol) of **4** were dissolved at ambient temperature and stirred for two hours. The solution was filtered, concentrated to half the volume and cooled to -20^{o}C, yielding 1.82 g (7.4 mmol, 81%) of **2** as red crystals.

^{1}H NMR (200 MHz, C_6D_6, 25^{o}C): δ 3.41 (s, 12H, NCH_3), 1.31 (s, 9H, *t*-Bu). *$^{13}C\{^{1}H\}$ NMR* (50.3 MHz, C_6D_6, 25^{o}C): δ 50.9 (NCH_3), 30.6 (CH_3 of *t*-Bu), C_q of *t*-Bu not observed. *^{51}V NMR* (78.9 MHz, C_6D_6, 25^{o}C): δ -281 (t, $J_{V\text{-}N}$ = 91). *IR* (nujol): 951 (s), 1030 (w), 1045 (w), 1157 (w),

1211 (w), 1233 (s), 1358 (w), 1412 (w) cm^{-1}. *Anal. Calcd (%) for $C_8H_{21}N_3VCl$*: C: 39.11, H: 8.62, N: 17.10, V: 20.74, Cl: 14.43; Found: C: 38.99, H: 8.57, N: 16.79, V: 20.62, Cl: 14.09.

Synthesis of (*t*-BuN)$VCl_2(NMe_2)$ (**3**)

In 100 mL of pentane 2.46 g (10.8 mmol) of **4** was dissolved and 0.55 g (10.8 mmol) of $LiNMe_2$ was added. The color of the solution quickly changed from orange to brown, and the solution was stirred for one hour. After filtration the brown solution was concentrated to half the volume and cooled to -25°C, which yielded 1.20 g (5.08 mmol, 47%) of **3** as red crystals.

^1H NMR (200 MHz, C_6D_6, 25°C): δ 3.65 (br, 3H, NCH_3), 3.43 (br, 3H, NCH_3), 1.20 (s, 9H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (50.3 MHz, C_6D_6, 25°C): δ 47.3 (NCH_3), 29.3 (CH_3 of *t*-Bu), C_q of *t*-Bu not observed. *^{51}V NMR* (78.9 MHz, C_6D_6, 25°C): δ -153 ($\Delta\nu_{1/2}$ = 320). *IR* (nujol): 939 (w), 1163 (w), 1213 (s), 1227 (s) cm^{-1}. *Anal. Calcd (%) for $C_6H_{15}N_2VCl_2$*: C: 30.40, H: 6.38, N: 11.73, V: 21.49, Cl: 29.91; Found: C: 30.38, H: 6.22, N: 11.73, V: 21.33, Cl: 29.61.

Synthesis of ($C_5H_4CH_2CH_2NMe$)VCl(N*t*-Bu) (**5**)

To a solution of 0.95 g (3.9 mmol) of **2** in 20 mL of pentane 0.49 g (4.0 mmol) of $C_5H_5(CH_2)_2N(H)Me$ was added. The brown solution was refluxed for 18 hours, after which the color had changed to red. All volatiles were removed *in vacuo* and the resulting solid was extracted twice with 10 mL of pentane. The pentane solution was concentrated and cooled to -20 °C, yielding 0.80 g (2.9 mmol, 74%) of **5** as red crystals.

^1H NMR (500 MHz, C_6D_6, 25°C): δ 6.11 (m, 1H, Cp), 5.88 (m, 2H, Cp), 5.11 (m, 1H, Cp), 4.60 (m, 1H, NC*H*H), 4.01 (s, 3H, NCH_3), 3.20 (m, 1H, NCH*H*), 2.46 (m, 1H, CpC*H*H), 1.98 (m, 1H,CpCH*H*), 1.19 (s, 9H, *t*-Bu). *$^{13}C\{^1H\}$ NMR* (125.7 MHz, C_6D_6, 25°C): δ 137.5 (C_{ipso} of Cp), 116.2, 111.7, 100.6, 99.6 (4 CH of Cp), 81.6 (NCH_3), 61.6 (NCH_2), 30.9 (CH_3 of *t*-Bu), 28.3 ($CpCH_2$). *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -679 ($\Delta\nu_{1/2}$ = 350). *Anal. Calcd (%) for $C_{12}H_{20}N_2VCl$*: C: 51.72, H: 7.23, N: 10.05, found: C: 51.28, H: 7.37, N: 9.99.

Synthesis of ($C_5H_4CH_2CH_2N$*i*-Pr)VCl(N*t*-Bu) (**6**)

To a solution of 3.26 g (13 mmol) of **2** in 100 mL of pentane 2.00 g (13 mmol) of $C_5H_5(CH_2)_2N(H)$*i*-Pr was added. The brown solution was refluxed for 18 hours, after which the color had changed to red. All volatiles were removed *in vacuo* and the resulting solid was extracted twice with 50 mL of pentane. The pentane solution was concentrated and cooled to -20 °C, yielding 3.31 g (10.8 mmol, 83%) of **6** as red crystals.

^1H NMR (300 MHz, C_6D_6, 25°C): δ 6.10 (m, 1H, Cp), 5.97 (m, 2H, Cp and CH of *i*-Pr), 5.87 (m, 1H, Cp), 5.13 (m, 1H, Cp), 4.66 (m, 1H, NC*H*H), 3.25 (dd, J_{H-H} = 6 / 13, 1H, NCH*H*), 2.47 (m, 1H, CpC*H*H), 1.76 (m, 1H,CpCH*H*), 1.19 (s, 9H, *t*-Bu), 1.01 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.98 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *$^{13}C\{^1H\}$ NMR* (75.4 MHz, C_6D_6, 25°C): δ 139.6 (C_{ipso} of Cp), 115.1, 114.6, 100.5, 99.5 (4 CH of Cp), 72.3 (CH of *i*-Pr), 70.5 (NCH_2), 30.0 ($CpCH_2$), 31.2

(CH_3 of *t*-Bu), 21.2, 20.5 (2 CH_3 of *i*-Pr), C_q of *t*-Bu not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ -674 ($\Delta\nu_{½}$ = 360). *IR*: 652 (w), 810 (s), 837 (w), 876 (w), 1146 (w), 1169 (w), 1209 (s), 1225 (s), 1356 (s) cm^{-1}. *Anal. Calcd (%) for $C_{14}H_{24}N_2VCl$*: C: 54.82, H: 7.89, N: 9.13, V: 16.61, Cl: 11.56, found: C: 54.64, H: 7.92, N: 8.96, V: 16.45, Cl: 11.46.

Synthesis of ($C_5H_4CH_2CH_2CH_2N$*i*-Pr)VCl(N*t*-Bu) (**7**)

To a solution of 0.27 g (1.5 mmol) $C_5H_5(CH_2)_3N(H)$*i*-Pr in 5 mL THF was added 0.15 g (1.6 mmol) Me_3SiCH_2Li. The solution was stirred for half an hour and then added to a solution of 0.34 g (1.5 mmol) of **4** in 20 mL of THF, cooled to 0°C. The solution was brought to room temperature and stirred for an additional hour. All volatiles were removed *in vacuo*, and the brown solid was extracted twice with 10 mL of pentane. After removal of the solvent 0.18 g (0.56 mmol, 37%) of **7** is obtained as a red oil. ^{1}H NMR shows small amounts of impurities in the range of 0 - 2 ppm.

^1H *NMR* (500 MHz, C_6D_6, 25°C): δ 6.26 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 6.04 (m, 1H, Cp), 5.92 (m, 1H, Cp), 5.76 (m, 1H, Cp), 4.96 (m, 1H, Cp), 3.22 (dd, J_{H-H} = 16 / 8, 1H, NC*H*H), 2.87 (dd, J_{H-H} = 15 / 8, 1H, NCH*H*), 2.30 (m, 1H, CpC*H*H), 2.16 (m, 1H, CpCH*H*), 1.89 (m, 1H, CH_2C*H*H), 1.44 (m, 1H, CH_2CH*H*), 1.28 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 1.18 (s, 9H, *t*-Bu), 0.96 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). $^{13}C\ \{^1H\}$ *NMR* (125.7 MHz, C_6D_6, 25°C): δ 117.7 (C_{ipso} of Cp), 114.4, 102.2, 97.2, 94.8 (4 CH of Cp), 72.2 (CH of *i*-Pr), 48.9 (NCH_2), 28.1 ($CpCH_2$), 25.6 (CH_3 of *t*-Bu), 22.0 ($CH_2CH_2CH_2$), 16.5, 15.6 (2 CH_3 of *i*-Pr), C_q of *t*-Bu not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ -708 ($\Delta\nu_{½}$ = 380).

Synthesis of ($C_5H_4CH_2CH_2N$*i*-Pr)VCl(N*p*-Tol) (**8**)

In 20 mL of toluene 0.45 g (1.5 mmol) of **6** and 0.17 g (1.6 mmol) of *p*-toluidine were dissolved. The brown solution was refluxed for 30 hours, during which it was regularly degassed to remove the formed *t*-$BuNH_2$, after which all volatiles were removed *in vacuo*. The resulting dark solid was stripped of residual toluene by addition of 2 x 10 mL of ether and subsequent removal *in vacuo*. Extraction of the resulting dark solid with 2 x 20 mL of ether gave a dark red solution, which after cooling to -25°C yielded 0.40 g (1.18 mmol, 78%) of **8** as dark red crystals.

^1H *NMR* (500 MHz, C_6D_6, 25°C): δ 7.15 (overlap with solvent, CH of *p*-Tol), 6.81 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 6.20 (m, 1H, Cp), 5.96 (m, 1H, Cp), 5.61 (m, 1H, Cp), 5.54 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.15 (m, 1H, Cp), 4.70 (m, 1H, NC*H*H), 3.33 (ddd, J_{H-H} = 14 / 7 / 3, 1H, NCH*H*), 2.49 (ddd, J_{H-H} = 13 / 7 / 2, 1H, CpC*H*H), 2.05 (s, 3H, CH_3 of *p*-Tol), 1.86 (m, 1H, CpCH*H*), 1.13 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.97 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). $^{13}C\ \{^1H\}$ *NMR* (125.7 MHz, C_6D_6, 25°C): δ 139.1 (C_{ipso} of Cp), 135.4 (C_{ipso} of *p*-Tol), 129.1, 125.5 (2 CH of *p*-Tol), 115.4, 113.9, 103.9, 100.7 (4 CH of Cp), 72.1 (NCH_2), 71.1 (CH of *i*-Pr), 29.5 ($CpCH_2$), 22.2 (CH_3 of *i*-Pr), 21.2 (CH_3 of *p*-Tol), 21.1 (CH_3 of *i*-Pr), C_q of *p*-Tol not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ

-579 ($\Delta\nu_{½}$ = 500). *Anal. Calcd (%) for $C_{17}H_{22}N_2VCl$*: C: 59.92, H: 6.51, N: 8.22, V: 14.95, Cl: 10.40, found: C: 59.85, H: 6.51, N: 8.16, V: 14.86, Cl: 10.46.

Synthesis of $(C_5H_4CH_2CH_2NMe)VMe(N$*t*-Bu) (**9**)

To a solution of 1.18 g (4.2 mmol) of **5** in 30 mL of Et_2O and 5 mL of toluene was added 2.8 mL of 1.53 M MeLi in Et_2O (4.3 mmol). The solution was stirred for half an hour, after which all volatile compounds were removed *in vacuo*. The resulting red oil was stripped of residual toluene by addition of 2 x 5 mL of pentane and subsequent removal *in vacuo*. Extraction with 2 x 20 mL of pentane and removal of the solvent *in vacuo* yielded 0.89 g of **9** as a red oil. ^{1}H NMR showed small amounts of impurities in the region of 0 - 4 ppm. Crude yield: 3.4 mmol (81%).

^{1}H NMR (500 MHz, C_6D_5Br, 25^{o}C): δ 5.94 (br, 1H, Cp), 5.63 (br, 1H, Cp), 5.53 (br, 1H, Cp), 5.34 (br, 1H, Cp), 4.15 (m, 1H, NC*H*H), 3.79 (s, 3H, NCH_3), 3.47 (m, 1H, NCH*H*), 2.57 (m, 1H, CpC*H*H), 2.40 (m, 1H,CpCH*H*), 1.23 (s, 9H, *t*-Bu), 0.63 (br, $\Delta\nu_{½}$ = 12, 3H, VCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, 25^{o}C): δ 133.9 (C_{ipso} of Cp), 114.7, 106.1, 102.3, 98.3 (4 CH of Cp), 78.6 (NCH_3), 58.9 (NCH_2), 32.2 (CH_3 of *t*-Bu), 29.1 ($CpCH_2$) C_q of *p*-Tol and VCH_3 not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25^{o}C): δ -679 ($\Delta\nu_{½}$ = 700).

Synthesis of $(C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*t*-Bu) (**10**)

To a solution of 1.14 g (3.7 mmol) of **6** in 20 mL of pentane was added 4.5 mL of 0.88 M MeLi in Et_2O (4.0 mmol). The solution was stirred for an hour, after which all volatile compounds were removed *in vacuo*. The resulting brown solid was extracted twice with 30 mL of pentane and concentrated to ~10 mL. Cooling to -60^{o}C yielded 0.50 g (1.8 mmol, 49%) of analytically pure **10** as a red brown crystals. Recrystallization from pentane produced crystals of **10**, suitable for X-ray diffraction.

^{1}H NMR (300 MHz, C_6D_6, 25^{o}C): δ 5.83 (m, 1H, Cp), 5.50 (m, 1H, Cp), 5.41 (m, 2H, Cp), 5.29 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 4.13 (m, 1H, NC*H*H), 3.30 (m, 1H, NCH*H*), 2.50 (ddd, J_{H-H} = 3 / 7 / 13, 1H, CpC*H*H), 2.07 (m, 1H, CpCH*H*), 1.25 (s, 9H, *t*-Bu), 1.15 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.95 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.69 (br, $\Delta\nu_{½}$ = 8, 3H, VCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_7D_8, -70^{o}C): δ 132.9 (C_{ipso} of Cp), 112.7, 107.5, 100.6, 94.1 (4 CH of Cp), 70.4 (C_q of *t*-Bu), 67.1 (CH of *i*-Pr), 66.5 (NCH_2), 29.4 ($CpCH_2$), 31.2 (CH_3 of *t*-Bu), 21.8, 20.7 (2 CH_3 of *i*-Pr), 17.7 (br, $\Delta\nu_{½}$ = 75, VCH_3). *^{13}C NMR* (125.7 MHz, C_6D_6, 25^{o}C): δ 132.3 (s, C_q of Cp), 113.0, 107.9, 100.9, 97.5 (d, J_{C-H} = 170, 172, 173, 173, 4 CH of Cp), 67.5 (d, 142, CH of *i*-Pr), 66.8 (t, 142, NCH_2), 31.6 (q, 126, CH_3 of *t*-Bu), 29.9 (t, 129, $CpCH_2$), 22.2 (q, 125, CH_3 of *i*-Pr), 21.1 (q, 125, CH_3 of *i*-Pr), 17 (very broad, VCH_3). C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25^{o}C): δ -665 ($\Delta\nu_{½}$ = 320). *IR*: 656 (w), 667 (w), 689 (w), 814 (s), 851 (w), 868 (w), 957 (w), 990 (w), 1018 (w), 1036 (w), 1044 (w), 1071 (w), 1115 (w), 1148 (w), 1173 (w), 1213 (w), 1248 (s), 1333 (w), 1358 (s) cm^{-1}. *Anal. Calcd (%) for $C_{15}H_{27}N_2V$*: C: 62.92, H: 9.50, N: 9.78, V: 17.79; found: C: 62.66, H: 9.49, N: 9.80, V: 17.68.

Synthesis of ($C_5H_4CH_2CH_2N$*i*-Pr)V(CH_2CMe_3)(N*t*-Bu) (**11**)

To a solution of 0.34 g (1.1 mmol) of **6** in 20 mL of pentane was added 0.10 g (1.2 mmol) of $LiCH_2CMe_3$. The solution is stirred for half an hour, after which all volatiles were removed *in vacuo*. The red residue is extracted with 30 mL of pentane. After removal of the solvent 0.33 g of **11** is obtained as a red oil. ^{1}H NMR shows small amounts of impurities in the range of 0 - 2 ppm. Crude yield: 0.96 mmol (87%).

^{1}H NMR (300 MHz, C_6D_6, 25°C): δ 5.73 (m, 1H, Cp), 5.64 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.44 (m, 1H, Cp), 5.31 (m, 2H, Cp), 4.29 (m, 1H, NC*H*H), 3.18 (m, 1H, NCH*H*), 2.46 (dd, J_{H-H} = 6 / 13, 1H, CpC*H*H), 1.93 (m, 1H, CpCH*H*), 1.56 (m, 2H, VCH_2), 1.36 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu), 1.06 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.93 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_7D_8, -70°C): δ 134.0 (C_{ipso} of Cp), 112.1, 109.8, 99.0, 97.5 (4 CH of Cp), 70.9 ($\Delta\nu_{½}$ = 22, C_{quart} of *t*-Bu), 69.1 (CH of *i*-Pr), 65.3 (NCH_2), 62.0 ($\Delta\nu_{½}$ = 67, VCH_2), 34.3, 31.6 (CH_3 of 2 *t*-Bu), 30.2 ($CpCH_2$), 22.8, 20.3 (2 CH_3 of *i*-Pr). *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -579 ($\Delta\nu_{½}$ = 330). *IR* (neat): 654 (w), 689 (w), 812 (s), 851 (w), 864 (w), 953 (w), 978 (w), 1007 (w), 1036 (w), 1045 (w), 1080 (w), 1105 (w), 1146 (w), 1173 (w), 1209 (w), 1238 (s), 1310 (w), 1331 (w), 1354 (s), 1375 (w), 1397 (w), 1454 (s), 2864 (s), 2893 (s), 2940 (s), 2967 (s), 3106 (w) cm^{-1}.

Synthesis of ($C_5H_4CH_2CH_2N$*i*-Pr)V(CH_2CMe_2Ph)(N*t*-Bu) (**12**)

To a solution of 0.42 g (1.4 mmol) of **6** in 20 mL of pentane was added 0.26 g (1.5 mmol) of $LiCH_2CMe_2Ph$. The solution is stirred for half an hour, after which all volatiles were removed *in vacuo*. The red residue is extracted with 30 mL of pentane. After removal of the solvent 0.59 g of **12** is obtained as a red oil. ^{1}H NMR shows impurities in the range of 0 - 7 ppm, with $PhCMe_3$ being the main impurity (~5%). Crude yield: 1.4 mmol (100%).

^{1}H NMR (300 MHz, C_6D_6, 25°C): δ 7.43 (m, 2H, Ph), 7.13 (m, 2H, Ph), 7.00 (m, 1H, Ph), 5.48 (br, 1H, Cp), 5.43 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.20 (br, 1H, Cp), 5.15 (br, 1H, Cp), 4.91 (m, 1H, Cp), 4.03 (m, 1H, NC*H*H), 3.00 (m, 1H, NCH*H*), 2.26 (dd, J_{H-H} = 6 / 12, 1H, CpC*H*H), 1.77 (m, 3H, CpCH*H* and VCH_2), 1.54 (s, 3H, $C(CH_3)_2$), 1.44 (s, 3H, $C(CH_3)_2$),1.04 (s, 9H, *t*-Bu), 0.89 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.70 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_7D_8, -70°C): δ 152.1 (C_{ipso} of Ph), 133.8 (C_{ipso} of Cp), 125.9, 124.5, 107.7 (3 CH of Ph), 111.4, 108.9, 99.7, 97.1 (4 CH of Cp), 71.0 (C_{quart} of *t*-Bu), 68.8 (CH of *i*-Pr), 65.5 (NCH_2), 59.9 ($\Delta\nu_{½}$ = 100, VCH_2), 30.0 ($CpCH_2$), 34.1 (CH_3 of *t*-Bu), 33.8, 31.5 (2 $C(CH_3)_2$), 22.6, 20.0 (2 CH_3 of *i*-Pr). *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -596 ($\Delta\nu_{½}$ = 370). *IR* (neat):654 (w), 667 (w), 700 (s), 764 (s), 814 (s), 851 (w), 868 (w), 953 (w), 978 (w), 1009 (w), 1034 (w), 1044 (w), 1074 (w), 1107 (w), 1125 (w), 1144 (w), 1173 (w), 1188 (w), 1211 (w), 1233 (s), 1333 (w), 1358 (s), 1375 (w), 1447 (s), 1495 (s), 1601 (w), 2863 (s), 2926 (s), 2971 (s), 3023 (w), 3057 (w), 3086 (w) cm^{-1}.

Synthesis of ($C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*p*-Tol) (**13**)

To a solution of 0.54 g (1.6 mmol) of **8** in 15 mL of Et_2O and 5 mL of toluene was added 1.1 mL of 1.53 M MeLi in Et_2O (1.7 mmol). The solution was stirred for half an hour, after which all volatile compounds were removed *in vacuo*. The resulting brown oil was stripped of residual toluene by addition of 2 x 5 mL of pentane and subsequent removal *in vacuo*. Extraction with 2 x 10 mL of pentane and removal of the solvent *in vacuo* yielded 0.51 g of **13** as a red oil. ^{1}H NMR showed small amounts of impurities in the region of 0 - 3 ppm. Crude yield: 1.6 mmol (100%).

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.20 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 6.89 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 5.89 (m, 1H, Cp), 5.50 (m, 1H, Cp), 5.43 (m, 1H, Cp), 5.28 (m, 1H, Cp), 4.89 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 4.16 (m, 1H, NC*H*H), 3.38 (m, 1H, NCH*H*), 2.47 (m, 1H, CpC*H*H), 2.14 (overlap, CpCH*H*), 2.11 (s, 3H, CH_3 of *p*-Tol), 1.25 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 1.09 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.92 (br, $\Delta\nu_{½}$ = 7, 3H, VCH_3). *^{13}C NMR* (125.7 MHz, C_6D_6, 25°C): δ 133.3, 133.0 (s, C_{ipso} of Cp and C_{ipso} of *p*-Tol), 129.1, 125.4 (d, J_{C-H} = 156, 159, 2 CH of *p*-Tol), 113.9, 108.2, 102.4, 100.6 (d, J_{C-H} = 173, 173, 174, 174, 4 CH of Cp), 69.3 (t, J_{C-H} = 136, NCH_2), 66.8 (d, J_{C-H} = 138, CH of *i*-Pr), 29.4 (t, J_{C-H} = 129, $CpCH_2$), 23.3, 22.3, 21.2 (2 CH_3 of *i*-Pr and CH_3 of *p*-Tol), C_q of *p*-Tol and VCH_3 not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -571 ($\Delta\nu_{½}$ = 440).

Synthesis of $(C_5H_4CH_2CH_2CH_2N$*i*-Pr)VMe(N*t*-Bu) (**14**)

A solution of 0.09 g (0.28 mmol) of **7** in 10 mL of pentane was cooled to 0°C, after which 0.35 mL 0.88 M MeLi (0.31 mmol) in ether was added. The brown solution was stirred for an hour at room temperature, after which all volatiles were removed *in vacuo*. The sticky residue was extracted with 10 mL of pentane. Evaporation of the solvent yielded 0.07 g of **14** as a red oil. ^{1}H NMR showed small amounts of impurities in the region of 0 - 3 ppm. Crude yield: 0.23 mmol (82%).

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 5.91 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.61 (m, 1H, Cp), 5.52 (m, 1H, Cp), 5.20 (m, 2H, Cp), 2.86 (m, 1H, NC*H*H), 2.69 (m, 1H, NCH*H*), 2.20 (m, 2H, $CpCH_2$), 1.56 (m, 1H, CH_2C*H*H), 1.44 (m, 1H, CH_2CH*H*), 1.18 (s, 9H, *t*-Bu), 1.12 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 1.06 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.68 (br, $\Delta\nu_{½}$ = 18, 3H, VCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_6, 25°C): δ 115.4 (C_{ipso} of Cp), 109.0, 99.6, 95.3, 94.0 (4 CH of Cp), 67.8 (CH of *i*-Pr), 45.9 (NCH_2), 29.6 ($CpCH_2$), 26.3 (CH_3 of *t*-Bu), 22.5 ($CH_2CH_2CH_2$), 17.3, 15.5 (2 CH_3 of *i*-Pr), C_q of *t*-Bu and VCH_3 not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -701 ($\Delta\nu_{½}$ = 450).

Synthesis of $[(C_5H_4CH_2CH_2N$*i*-Pr)V(μ-N*t*-Bu)$]_2$ (**15**)

To a solution of 0.27 g (0.88 mmol) of **6** in 20 mL of Et_2O was added 1.6 mL of 0.56 M EtMgCl in Et_2O (0.90 mmol). The solution immediately turned brown and was stirred for half an hour, during which it turned dark purple. All volatile compounds were removed *in vacuo* and the resulting dark solid was extracted with 2 x 30 mL of pentane. Concentrating and cooling the

solution to -25°C yielded 0.084 g of **15** as dark crystals. ^{1}H NMR showed impurities in the region of 0 - 7 ppm. Crude yield: 0.15 mmol (34%).

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 6.50 (br, 4H, Cp), 3.72 (t, J_{H-H} = 6, 4H, NCH_2), 3.56 (br, 4H, Cp), 2.76 (sept, J_{H-H} = 6, 2H, CH of *i*-Pr), 2.63 (t, J_{H-H} = 6, 4H, $CpCH_2$), 1.84 (s, 18H, CH_3 of *t*-Bu), 0.65 (d, J_{H-H} = 6, 12H, CH_3 of *i*-Pr). *^{13}C NMR* (125.7 MHz, C_6D_6, 25°C): δ 138.6 (s, C_{ipso} of Cp), 102.9, 100.5 (d, J_{C-H} = 171, 172, 2 CH of Cp), 64.7 (t, J_{C-H} = 133, NCH_2), 57.7 (d, J_{C-H} = 137, CH of *i*-Pr), 35.9 (q, J_{C-H} = 125, CH_3 of *t*-Bu), 30.7 (t, J_{C-H} = 127, $CpCH_2$), 21.2 (q, J_{C-H} = 124, CH_3 of *i*-Pr), C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ 137 ($\Delta\nu_{½}$ = 820).

Synthesis of (*p*-TolN)V(N*i*-Pr_2)Cl_2 (**18**)

To a suspension of 2.46 g (9.37 mmol) of **16** in 50 mL of ether 2.85 mL (28.1 mmol) of HN*i*-Pr_2 was added in five minutes. The suspension was stirred for 18 hours at room temperature, after which all volatiles were removed *in vacuo*. Extraction of the dark residue with 2 x 25 mL of ether, followed by concentration of the red solution and cooling to -25°C yielded 2.09 g (6.39 mmol, 68%) of **18** as red crystals.

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.26 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 6.58 (d, J_{H-H} = 9, 2H, CH of *p*-Tol), 5.89 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 3.01 (br, 1H, CH of *i*-Pr), 1.88 (s, 3H, CH_3 of *p*-Tol), 1.31 (d, J_{H-H} = 6, 6H, CH_3 of *i*-Pr), 0.87 (d, J_{H-H} = 6, 6H, CH_3 of *i*-Pr). *^{13}C NMR* (125.7 MHz, C_6D_6, 25°C): δ 138.6 (s, C_{ipso} of *p*-Tol), 129.2, 126.3 (d, J_{C-H} = 160, 163, 2 CH of *p*-Tol), 61.2, 55.7 (d, J_{C-H} = 138, 130, 2 CH of *i*-Pr), 28.5 (q, J_{C-H} = 128, CH_3 of *i*-Pr), 21.2 (q, J_{C-H} = 127, CH_3 of *p*-Tol), 18.8 (q, J_{C-H} = 127, CH_3 of *i*-Pr), C_q of *p*-Tol not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -67 (t, J_{V-N} = 96). *Anal. Calcd (%) for $C_{13}H_{21}N_2VCl$*: C: 47.73, H: 6.47, N: 8.56; found: C: 47.27, H: 6.42, N: 8.24.

Synthesis of (*p*-TolN)VCp(N*i*-Pr_2)Cl (**20**)

Onto 0.536 g (1.64 mmol) of **18** and 0.146 g (1.66 mmol) of CpNa, 30 mL of toluene was condensed at liquid nitrogen temperature. The mixture was thawed out and stirred for three hours at -40°C and for one night at room temperature, after which all volatiles were removed *in vacuo*. The resulting dark solid was stripped of residual toluene by addition of 2 x 5 mL of pentane and subsequent removal *in vacuo*. Extraction with 10 mL of pentane, concentration of the red solution and cooling to -25°C yielded 0.47 g (1.26 mmol, 77%) of **20** as red crystals.

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.19 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 6.78 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 5.83 (s, 5H, Cp), 4.96 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 3.33 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 2.03 (s, 3H, CH_3 of *p*-Tol), 1.85 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 1.25 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 1.04 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.74 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_6, 25°C): δ 136.0 (C_{ipso} of *p*-Tol), 129.2, 125.1 (2 CH of *p*-Tol), 108.6 (Cp), 65.0, 58.5 (2 CH of *i*-Pr), 31.1, 27.4 (2 CH_3 of *i*-Pr), 21.2 (CH_3 of *p*-Tol), 19.4, 17.6 (2 CH_3 of *i*-Pr), C_q

of *p*-Tol not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ -591 ($\Delta\nu_{½}$ = 400). *Anal. Calcd (%) for* $C_{18}H_{26}N_2VCl$: C: 60.59, H: 7.35, N: 7.85, Cl: 9.94; found: C: 60.45, H: 7.44, N: 7.87, Cl: 10.14.

Synthesis of (*t*-BuN)VCp_2(N*i*-Pr_2) (**21**)

To a mixture of 2.07 g (7.0 mmol) of **17** and 1.3 g (15 mmol) of CpNa 50 mL of cold THF (-30°C) was added and the resulting solution was stirred for one night at room temperature. After removal of all volatiles *in vacuo*, the dark residue was stripped of residual THF by addition of 2 x 10 mL of pentane and subsequent removal *in vacuo*. Extraction with 4 x 50 mL of pentane, followed by concentration of the red solution and cooling to -25°C yielded 2.12 g (6.57 mmol, 93%) of **21** as red crystals.

^{1}H *NMR* (500 MHz, THF-d_8, 50°C): δ 6.01 (br, 5H, Cp), 5.24 (br, 5H, Cp), 4.86 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 3.60 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 1.89 (br, 3H, CH_3 of *i*-Pr), 1.46 (s, 9H, *t*-Bu), 1.37 (br, 3H, CH_3 of *i*-Pr), 1.12 (d, J_{H-H} = 7, 6H, 2 CH_3 of *i*-Pr). ^{13}C *{*^{1}H*} NMR* (125.7 MHz, THF-d_8, 50°C): δ 116.8, 109.1 (2 Cp), 65.8, 56.7 (2 CH of *i*-Pr), 33.7 (CH_3 of *i*-Pr), 33.4 (CH_3 of *t*-Bu), 28.5, 22.2, 22.1 (3 CH of *i*-Pr), C_q of *t*-Bu not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ -623 ($\Delta\nu_{½}$ = 300). *Anal. Calcd (%) for* $C_{20}H_{33}N_2V$: C: 68.16, H: 9.44, N: 7.95, V: 14.57; found: C: 67.89, H: 9.67, N: 7.93, V: 14.30.

Synthesis of (*p*-TolN)VCp_2(N*i*-Pr_2) (**22**)

A suspension of 2.0 g (6.1 mmol) of **18** and 1.1 g (13 mmol) of CpNa in 40 mL of toluene was stirred for 18 hours at room temperature, after which all volatiles were removed *in vacuo*. Residual toluene was removed by addition of 2 x 5 mL of pentane and subsequent removal *in vacuo*. Extraction with 12 x 50 mL of pentane and cooling of the red solution to -25°C yielded 0.96 g (2.48 mmol, 41%) of **22** as red crystals.

^{1}H *NMR* (500 MHz, THF-d_8, 50°C): δ 7.18 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 7.05 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 6.05 (s, 5H, Cp), 5.22 (s, 5H, Cp), 4.91 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 3.66 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 2.32 (s, 3H, CH_3 of *p*-Tol), 1.89 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.37 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.16 (m, 6H, 2 CH_3 of *i*-Pr). ^{13}C *{*^{1}H*} NMR* (125.7 MHz, THF-d_8, 50°C): δ 136.7 (C_{ipso} of *p*-Tol), 130.7, 126.5 (2 CH of *p*-Tol), 117.0, 110.4 (2 Cp), 65.4, 58.7 (2 CH of *i*-Pr), 33.3, 28.3, 26.7, 22.2, 22.0 (4 CH_3 of *i*-Pr and CH_3 of *p*-Tol), C_q of *p*-Tol not observed. ^{51}V *NMR* (131.4 MHz, C_6D_6, 25°C): δ -546 ($\Delta\nu_{½}$ = 330). *Anal. Calcd (%) for* $C_{23}H_{31}N_2V$: C: 71.48, H: 8.09, N: 7.25, V: 13.18; found: C: 70.80, H: 7.86, N: 7.13, V: 12.93.

Synthesis of (*t*-BuN)VCp(N*i*-Pr_2)Me (**23**)

A solution of 0.57 g (1.77 mmol) of **19** in 25 mL of ether was cooled to -50°C, after which 1.2 mL 1.53 M MeLi (1.84 mmol) in ether was added. After stirring for 20 minutes at -10°C the color of the solution had changed from red to yellow. All volatiles were removed *in vacuo* and the resulting solid was stripped of residual ether by addition of 2 x 5 mL of cold pentane and

subsequent removal *in vacuo* at -10°C. Extraction with 30 mL of cold pentane and slow removal of the solvent *in vacuo* at -10°C yielded 0.47 g (1.55 mmol, 88%) of **23** as a yellow oil, which crystallized at -35°C. ^{1}H NMR of the yellow crystals showed no impurities.

^{1}H NMR (500 MHz, $C_6D_5CD_3$, -50°C): δ 5.58 (s, 5H, Cp), 4.29 (m, 1H, CH of *i*-Pr), 3.09 (br, 1H, CH of *i*-Pr), 1.76 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.38 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.23 (s, 9H, *t*-Bu), 0.83 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.80 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.62 (s, 3H, VCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, $C_6D_5CD_3$, -50°C): δ 104.6 (Cp), 62.0, 52.6 (2 CH of *i*-Pr), 32.2 (CH_3 of *i*-Pr), 31.5 (CH_3 of *t*-Bu), 27.1, 20.1, 19.1 (3 CH_3 of *i*-Pr), C_q of *t*-Bu and VCH_3 not observed. *^{51}V NMR* (131.4 MHz, $C_6D_5CD_3$, 25°C): δ -673 (t, J_{N-V} = 89).

Synthesis of (*p*-TolN)VCp(N*i*-Pr$_2$)Me (**24**)

A solution of 0.42 g (1.18 mmol) of **20** in 30 mL of ether was cooled to -40°C, after which 0.77 mL 1.53 M MeLi (1.18 mmol) in ether was added. After stirring for 20 minutes at -10°C the color of the solution has changed from red to orange. All volatiles were removed *in vacuo* and the resulting solid was stripped of residual ether by addition of 2 x 5 mL of cold pentane and subsequent removal *in vacuo* at -10°C. Extraction with 30 mL of cold pentane and slow removal of the solvent *in vacuo* at -10°C yielded 0.204 g (0.61 mmol, 51%) of **24** as yellow crystals.

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.16 (overlap with solvent, CH of *p*-Tol), 6.86 (d, J_{H-H} = 8, 2H, CH of *p*-Tol), 5.59 (s, 5H, Cp), 4.36 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 3.21 (br, 1H, CH of *i*-Pr), 2.10 (s, 3H, CH_3 of *p*-Tol), 1.78 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.42 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.85 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.82 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.79 (br, $\Delta\nu_{1/2}$ = 16, 3H, VCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_6, 25°C): δ 131.6 (C_{ipso} of *p*-Tol), 127.0, 122.8 (2 CH of *p*-Tol), 103.9 (Cp), 59.6, 52.8 (2 CH of *i*-Pr), 30.0, 24.9 (2 CH_3 of *i*-Pr), 19.0 (CH_3 of *p*-Tol), 18.4, 16.9 (2 CH_3 of *i*-Pr), C_q of *p*-Tol and VCH_3 not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -600 ($\Delta\nu_{1/2}$ = 320). *Anal. Calcd (%) for $C_{19}H_{29}N_2V$*: C: 67.84, H: 8.69, N: 8.33, V: 15.14, found: C: 67.65, H: 9.03, N: 8.27, V: 15.09.

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